

INDUSTRIAL CHALLENGES FOR THE CONVERSION OF LIGNOCELLULOSIC MATERIALS

Would modularization work?

AGENDA

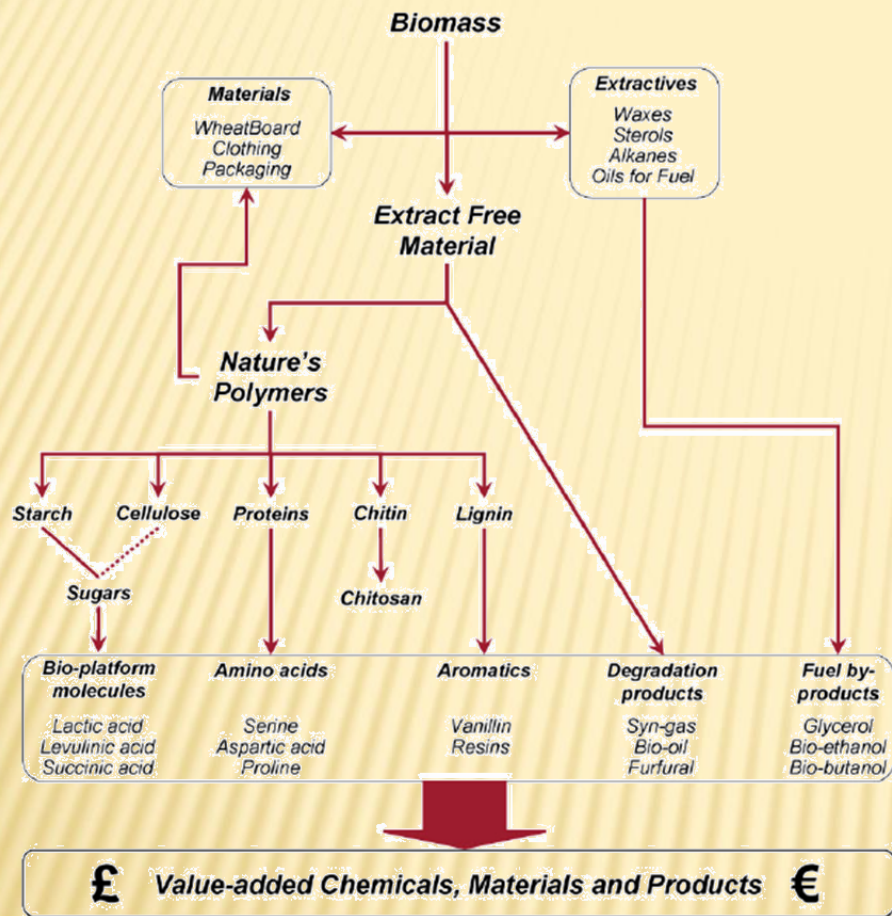
- Introduction
- Existing and emerging technologies
- Technical challenges
- Economical challenges
- Potential improvements



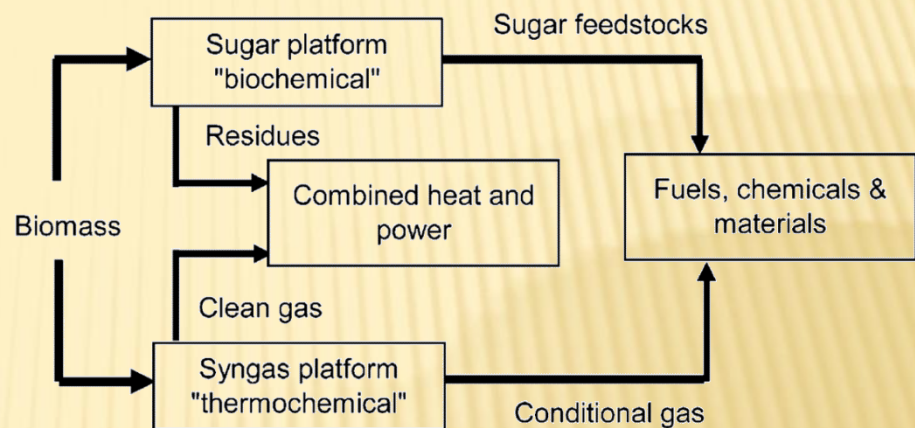
BIOMASS CONVERSION

Introduction

ORIGINS AND EVOLUTION



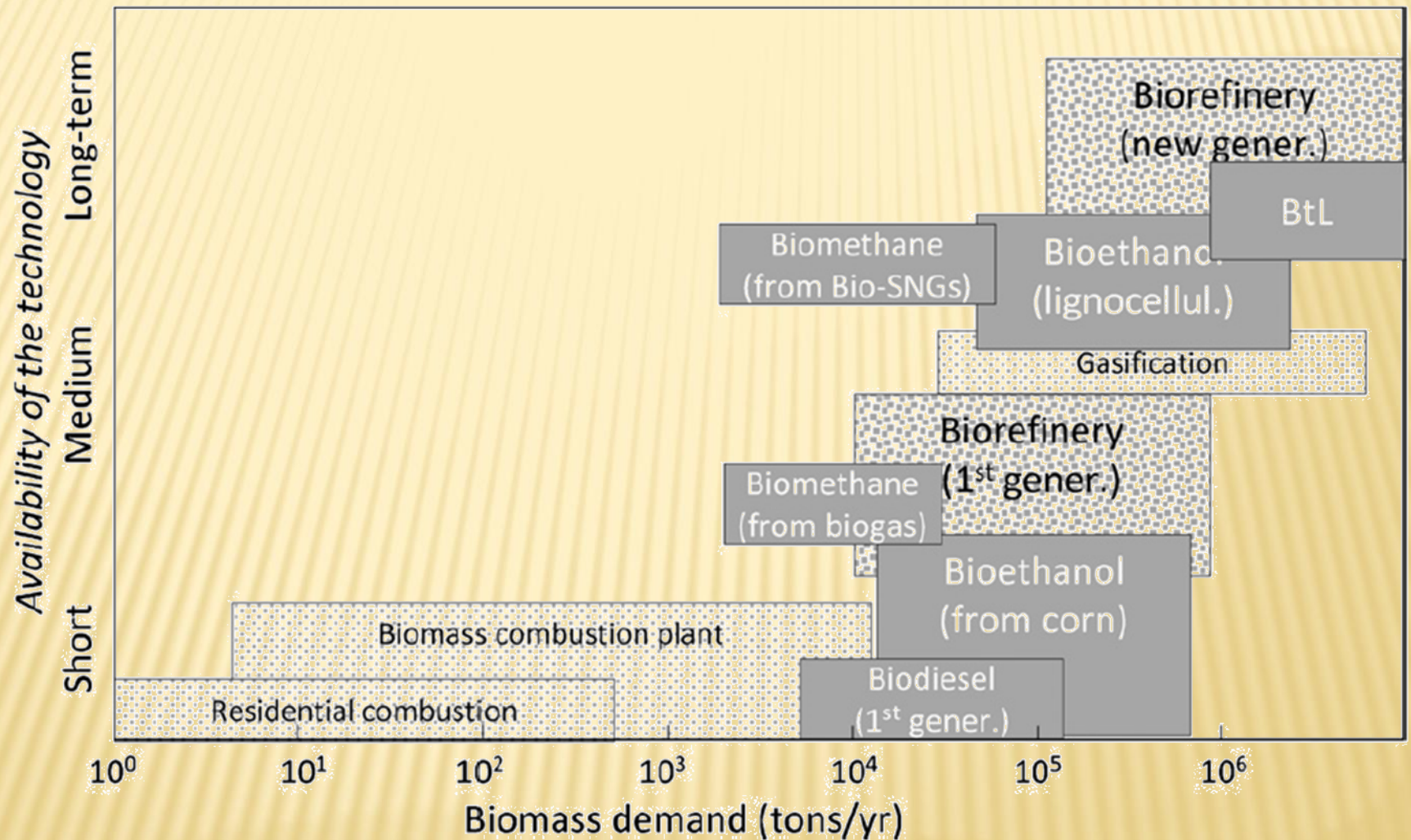
Source: J. H. Clark; F. E. I. Deswarte and T. J. Farmer.
Biofuels, Bioproducts and Biorefining 3 (2009) 72-90.



Source: S. Fernando; S. Adhikari; C. Chandrapal and N. Murali. *Energy & Fuels* 20 (2006) 1727-1737.

Generation	Feed	Examples
First	Sugars, starch, vegetable oils or animal fat	Bio-alcohols, hydrogenated vegetable oils (HVO), Biodiesel, bio-syngas, bio-gas
Second	Energy crops, agro- and forest residues, wood, organic waste	Bio-alcohols, bio-crude, bio-DMF, Bio-hydrogen, bio-Fischer Tropsch diesel, renewable fuels, "drop-in" fuels
Third	Algae	HVO, diesel

TECHNOLOGY NEEDS



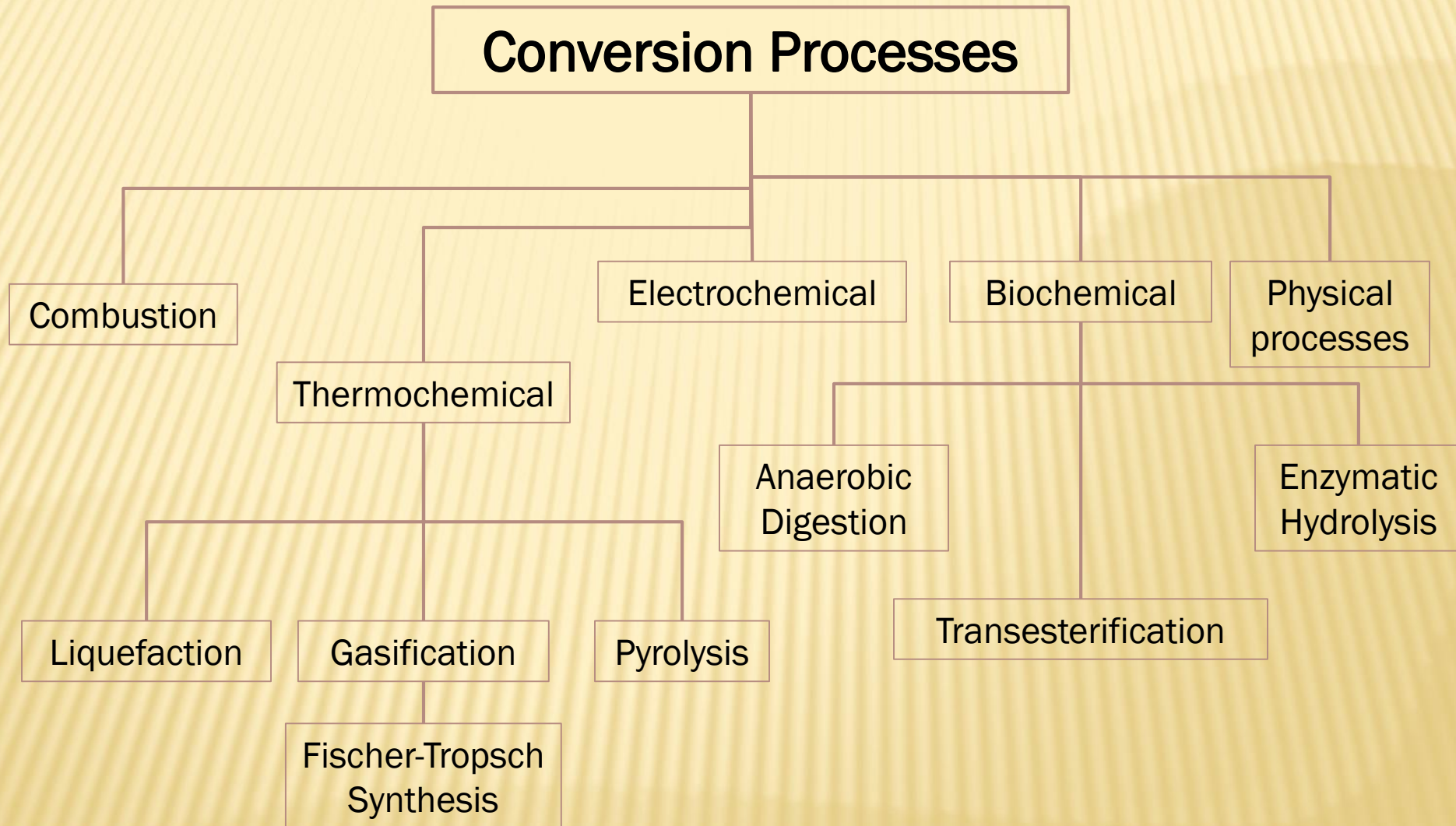
Source: G. Centi; P. Lanzafame and S. Perathoner. *Catalysis Today* 167 (2011) 14-30.



EXISTENT AND EMERGING TECHNOLOGIES

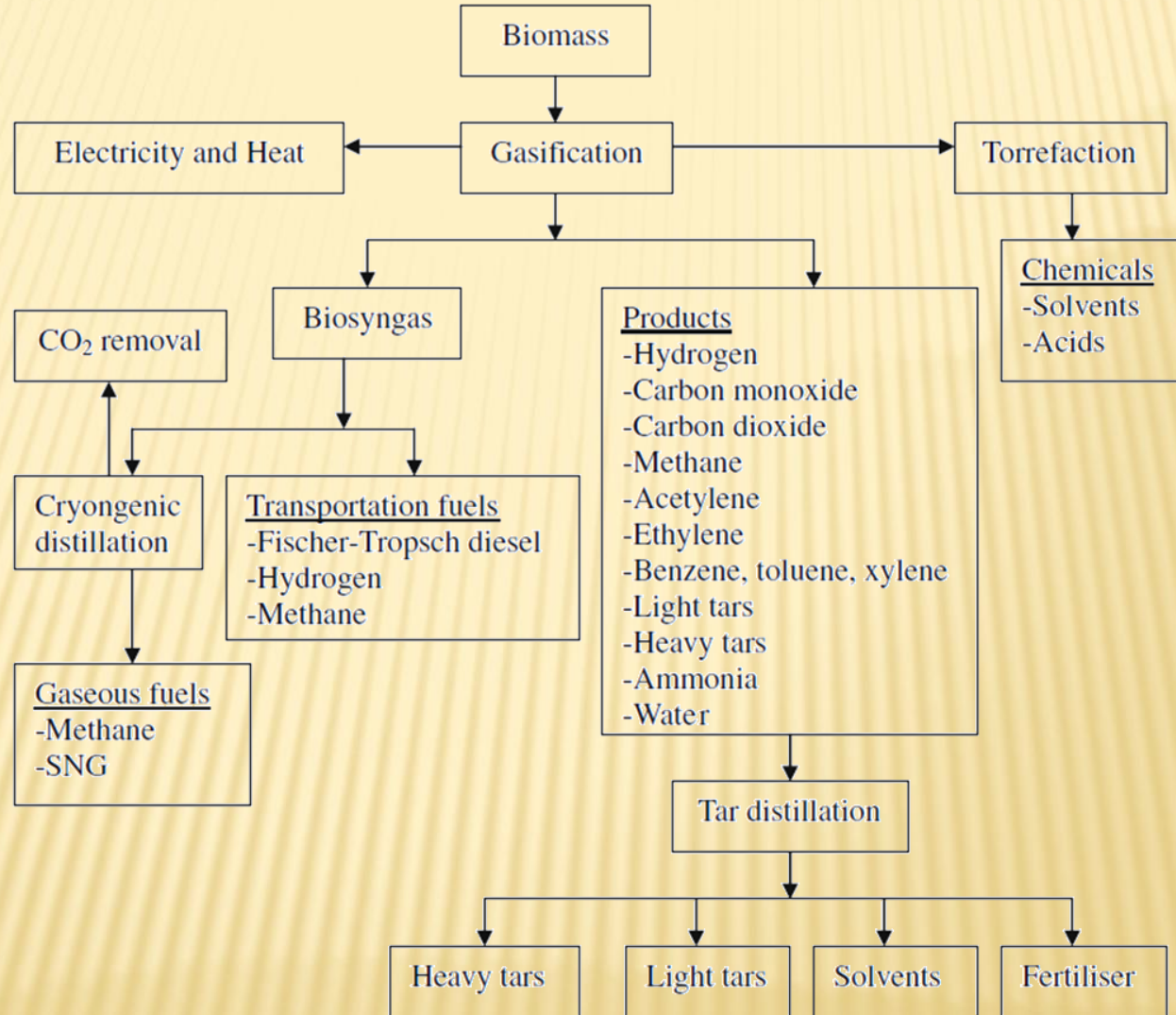
Renewable fuels and green chemicals production

SECOND GENERATION: OPTIONS



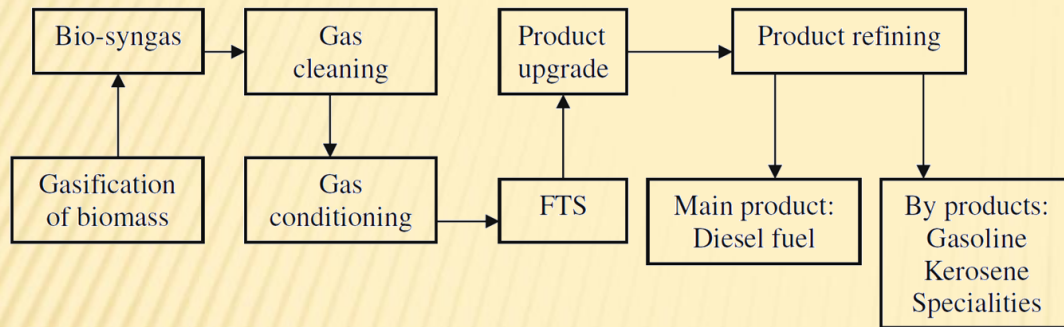
Adapted from A. Demirbas. *Energy Conversion and Management* 50 (2009) 2782-2801.

SYNGAS ROUTES: MATURE TECHNOLOGIES

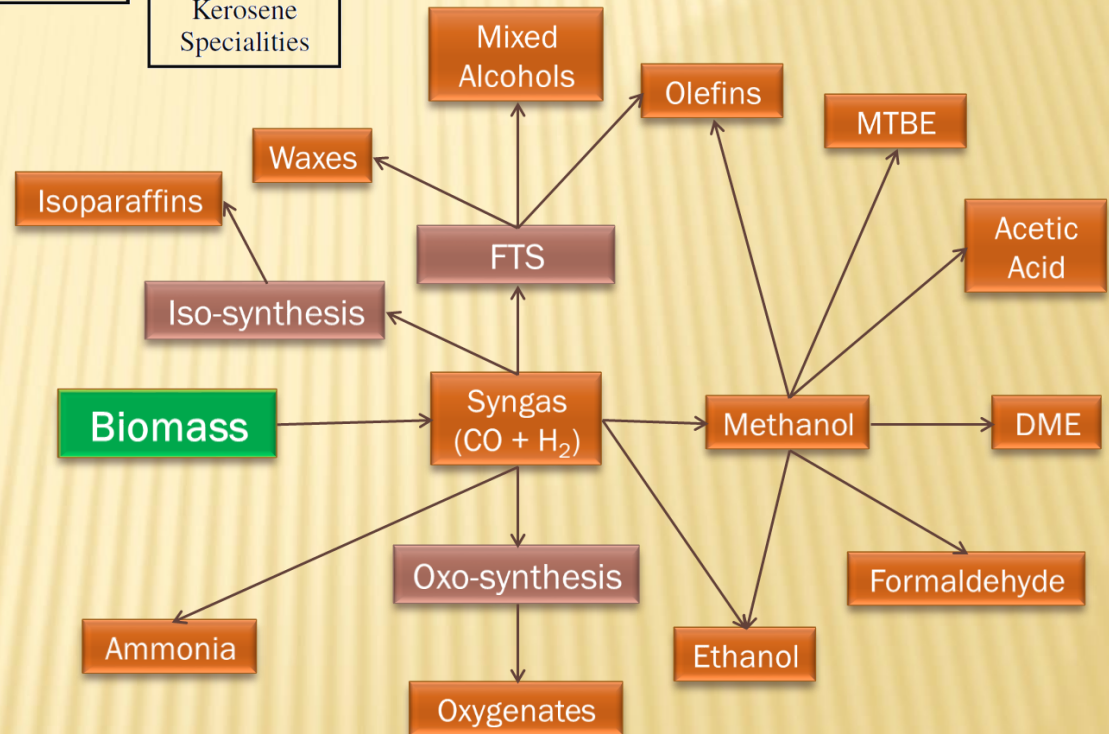


Source: A. Demirbas. *Energy Conversion and Management* 50 (2009) 2782-2801.

BIOFUELS & GREEN CHEMICALS VIA SYNGAS

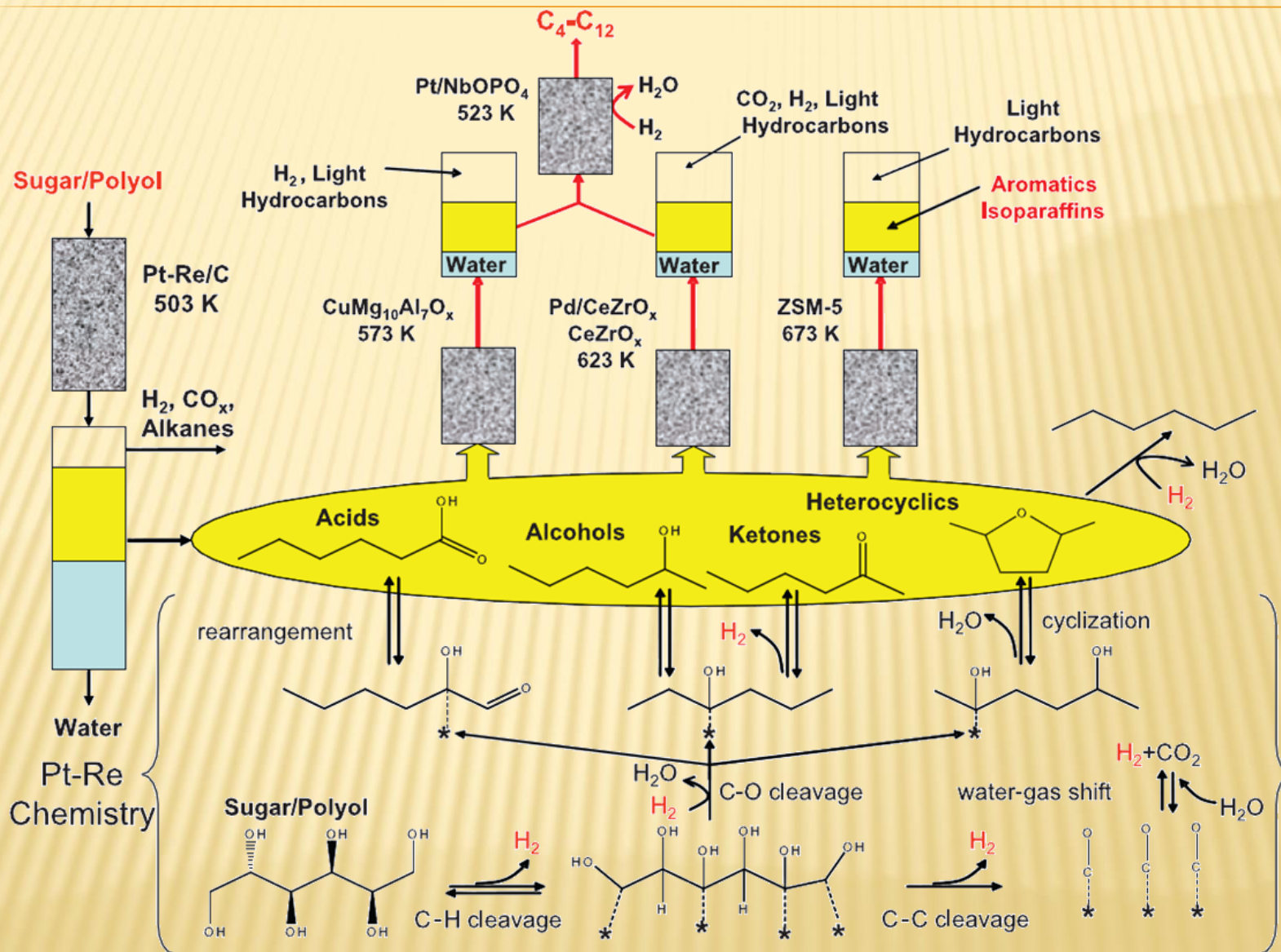


Source: M. F. Demirbas. *Applied Energy* 86 (2009) S151-S161.



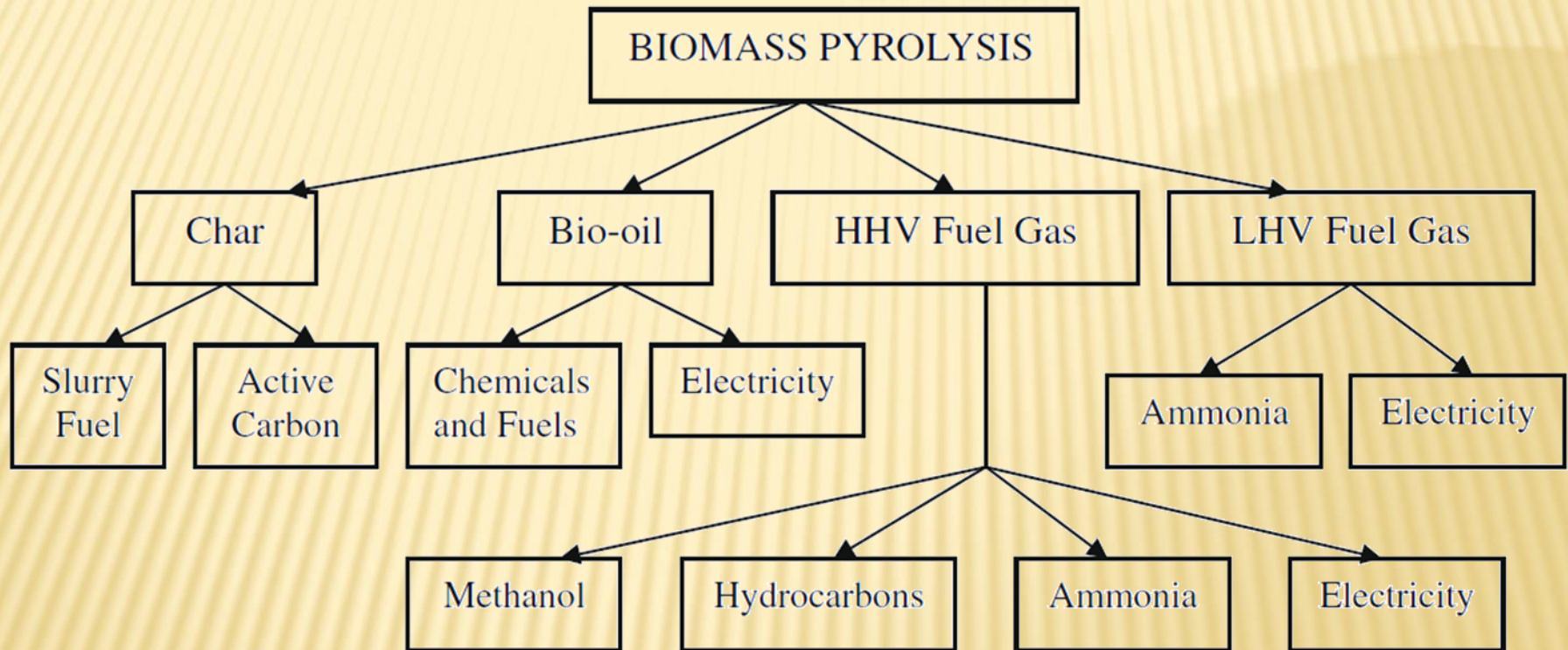
Adapted from: S. R. Decker; J. Sheehan; D. C. Dayton; J. J. Bozell; W. S. Adney; B. Hames; S. R. Thomas; R. L. Bain; S. Czernik; M. Zhang and M. E. Himmel in ***Handbook industrial chemistry & biotechnology***, ed. Kent, J.A. KENT & RIEGEL'S (2007), 1449-1538;

EMERGING TECHNOLOGIES: AQUEOUS PHASE CONVERSION



Source: G. W. Huber; J. N. Chheda; C. J. Barrett and J. A. Dumesic. *Science* 308 (2005) 1446-1450.

EMERGING TECHNOLOGIES: PYROLYSIS



Adapted from M. F. Demirbas. *Applied Energy* 86 (2009) S151-S161.

ACTORS

Company	Technology	Products
Anellotech	Thermocatalytic (scaling up)	Chemicals, specialties
Benefuels	Gasification / FTS (scaling up)	Syngas, lubes, specialties
Cool Planet Energy Sys.	Pyrolysis / Upgrading (R&D)	Charcoal, fuels
Elevance	Metathesis (commercial)	Polymers, additives, lubes
Empyro (BTG-True Power)	Pyrolysis (Demo)	Bio-crude
Enerken	Gasification / FTS (Demo)	Syngas, NH ₃ , CH ₃ OH, fuels, lubes
Envergent Tech.	Pyrolysis (scaling up)	Fuels
Fulcrum Bioenergy	Gasification / FTS / Upgrading	Syngas, fuels, chemicals
Green Envirotech	Electromagnetic Pyrolysis	Chemicals
Green Fuel Nordic Oy	Pyrolysis	Bio-crude
KiOR	Thermocatalytic / HDT (commercial)	Fuel blendstocks
Mercurius Biorefining	Hydrolysis / Cat upgrading	Fuels, chemicals
Midori	Cat-treatment in aq. phase	Sugars
NextFuels	Bio-liquefaction (R&D)	Bio-crude
Rennovia	Thermocatalytic (R&D)	Chemicals, specialties
Rive Tech.	Thermocatalytic (R&D)	Fuels, chemicals, specialties
Sundrop Fuels	Gasification / MTG (scaling up)	Gasoline, Kero
Virent	Thermocat. in aq. phase (Demo)	Fuels, chemicals
VTT-UPM-METSO	Integrated pyrolysis (R&D)	Bio-crude, energy
ZeaChem	Fermentation / Gasification	Ethanol, H ₂



TECHNICAL CHALLENGES

Known and exploited

LIGNOCELLULOSE

LIGNIN

- ✗ Complex aromatic structure
- ✗ High energetic content
- ✗ Resistant to biochemical conversion

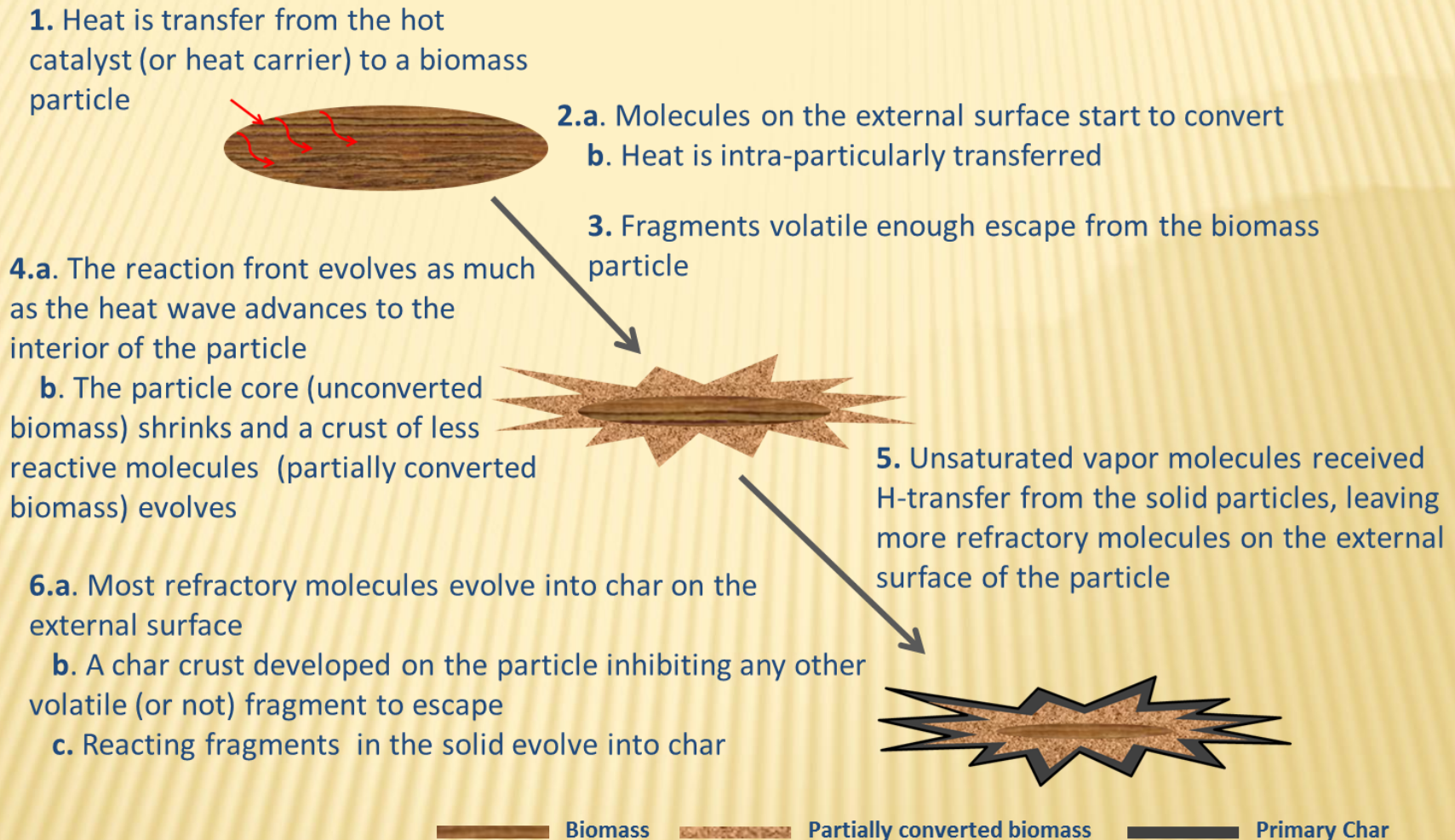
OTROS COMPONENTES

- ✗ Water
- ✗ 'Extractives'
- ✗ Minerals

SUGARS

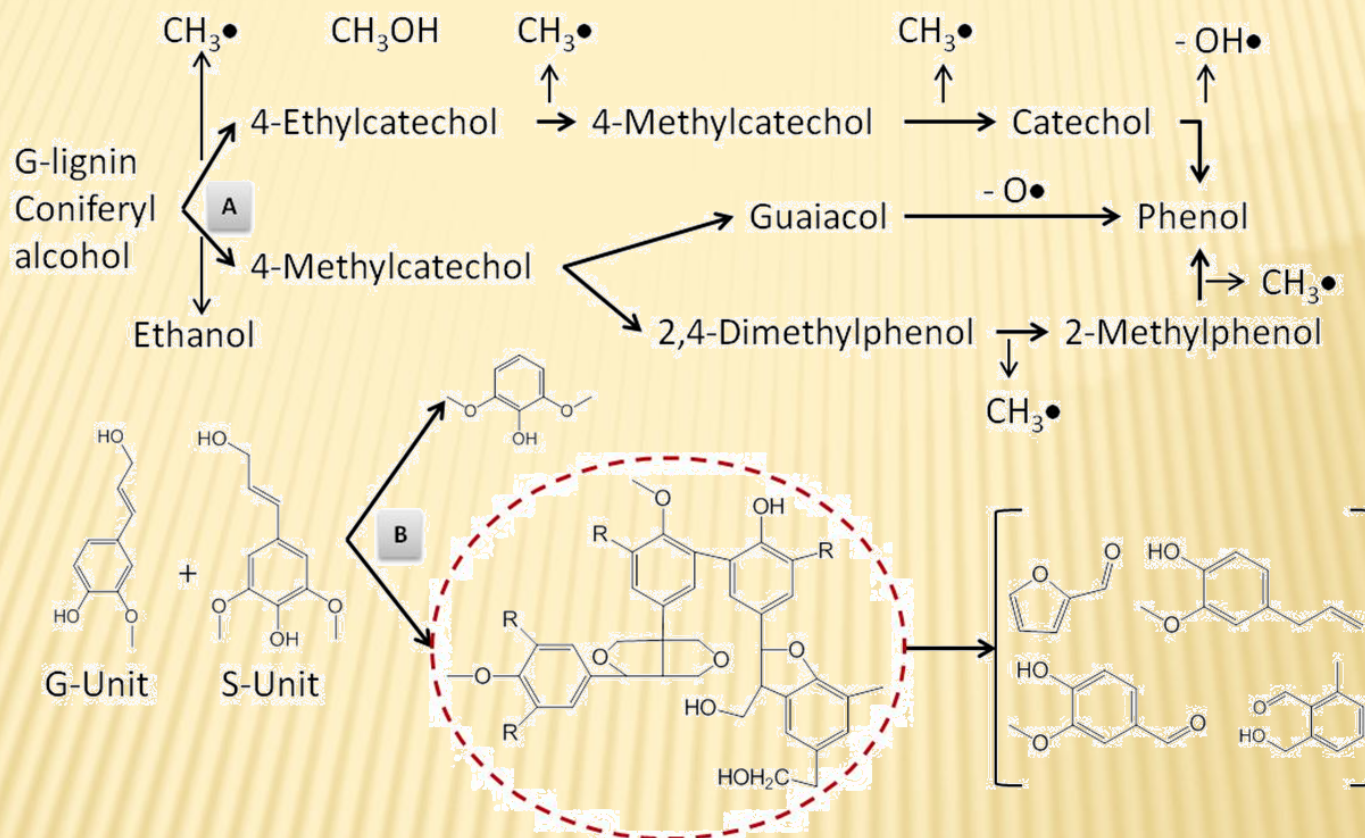
- ✗ Celullose
 - + Most abundant form of C
 - + Glucose polymer
 - + Biochemically converted
- ✗ Hemicelullose
 - + 2nd most abundant sugar
 - + C5 and C6 monomers
 - + Marginal biochemical conversion

PHYSICAL LIMITATIONS IN BIOMASS CONVERSION



How to cope with intra-particle heat transfer limitations?
How to minimize primary char formation?

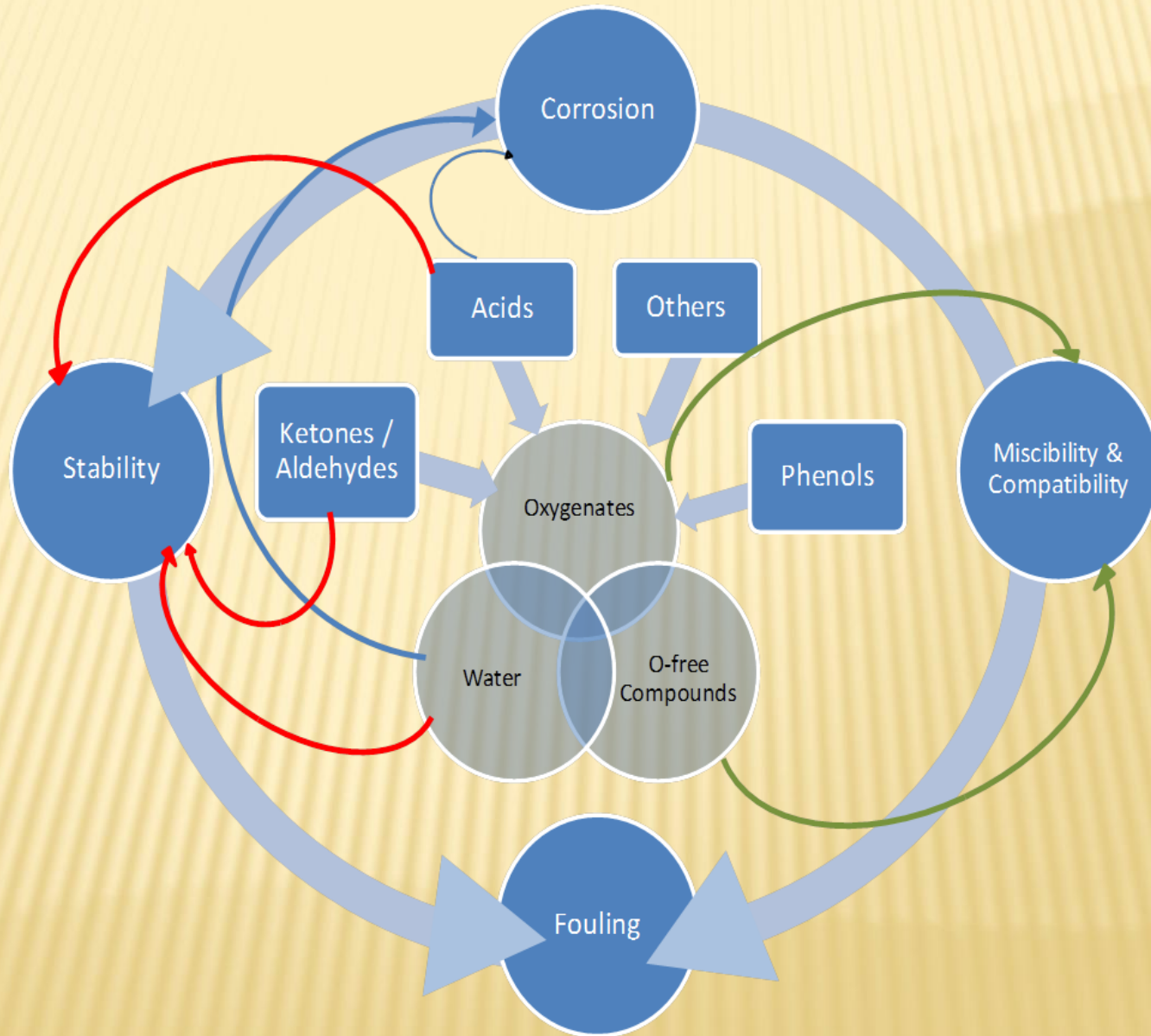
SECONDARY CHAR



Source: M. M. Ramirez-Corredores in ***The role of catalysis for the sustainable production of bio-fuels and bio-chemicals***, ed. Triantafyllidis, K., Lappas, A., and Stöcker, M. Elsevier, Amsterdam. (2013), 161-216. Adapted from: X. J. Guo; S. R. Wang; K. G. Wang and Z. Y. Luo. ***Chemical Research in Chinese Universities*** 27 (2011) 426-430.

Lignin reaction pathways indicate that G-units may form H-depleted free radical fragments, which might be char forming promoters/precursors.

PROCESSABILITY ISSUES





ECONOMICAL CHALLENGES

Needs for improving CapEx, OpEx and Revenues

BUSINESS VS. ENVIRONMENTAL CONSCIOUS?



1st generation biofuels

Biodiesel (rape)
Biodiesel (soya)
Biodiesel (palm)

EtOH (cereals)
EtOH (maize)
EtOH (sugar beet)

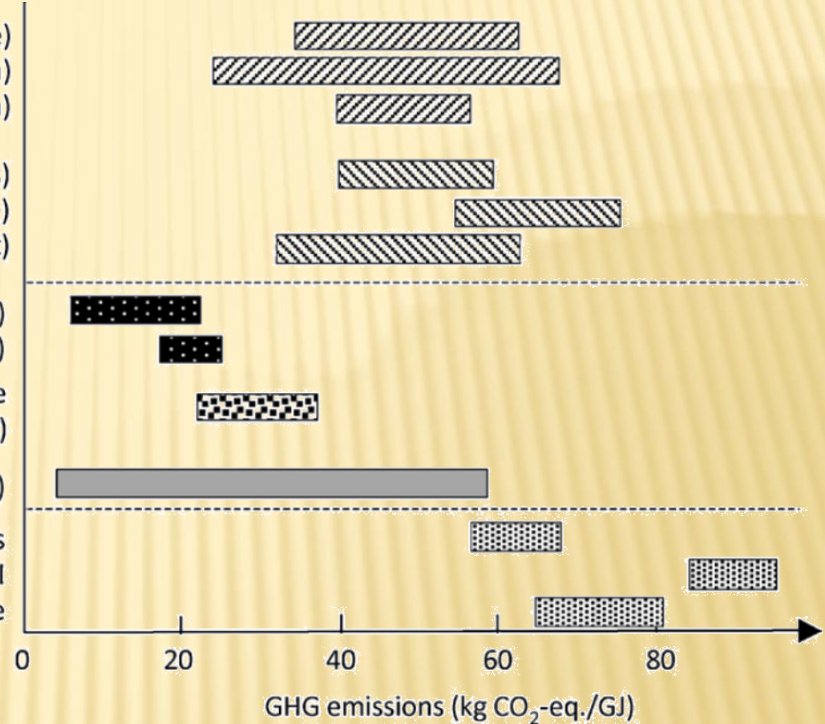
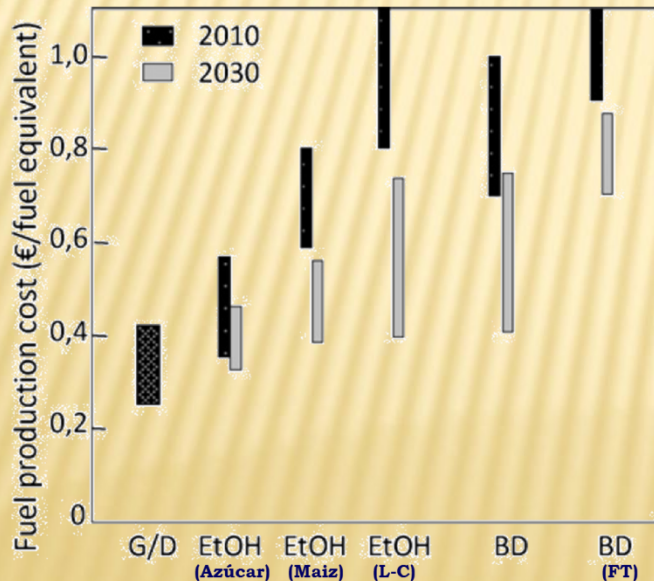
2nd generation biofuels

EtOH (ligno residues)
EtOH (ligno crops)
Hydrotreated Vegetable Oil (NExBTL)

FT fuels (from biomass)

Natural gas
Diesel
Gasoline

Fossil Fuels



Source: G. Centi; P. Lanzafame and S. Perathoner. *Catalysis Today* 167 (2011) 14-30.

CapEx: OPPORTUNITY NICHES

- ✗ Number of process units

- + Conversion / separation / fractionation
- + Throughput
- + Organics in aqueous phase

- ✗ Crude quality

- + Corrosivity
- + Unstable compounds
- + Miscibility / compatibility
- + Energy value



Process chemistry changes?

CapEx IMPROVING ROUTES

CURRENT UNITS

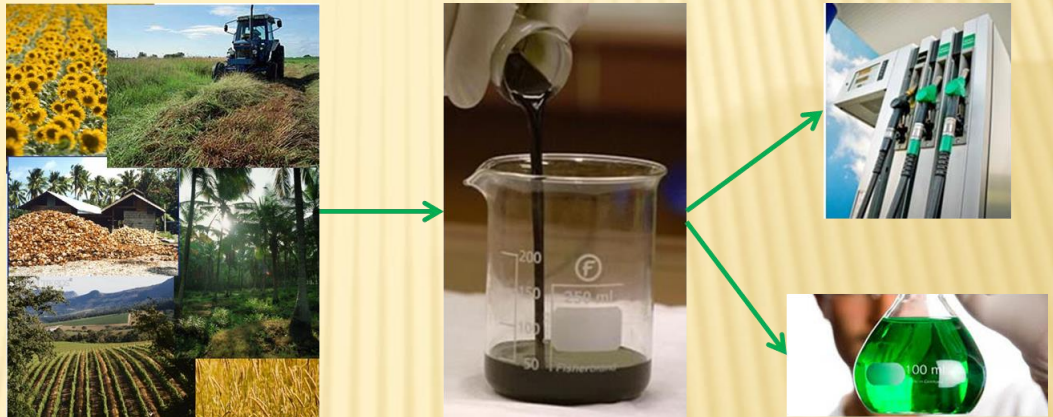
- ✖ Biomass pretreatment
- ✖ Feeder
- ✖ Converter
- ✖ Quenching
- ✖ Gas recovery
- ✖ Condensable vapors recovery
- ✖ Aqueous phase recovery
- ✖ Solids separation
- ✖ Organics upgrading (1 to 3 units: gas, aqueous and bio-oil)

APPROACHES

- ✖ Crude quality
 - + Recovery
 - + Acidity abatement
 - + Stability improvements
 - + Fungible oil
- ✖ New catalysts
- ✖ Process integration
- ✖ Process intensification
- ✖ Synergies

OpEx: OPPORTUNITY NICHES AND APPROACHES

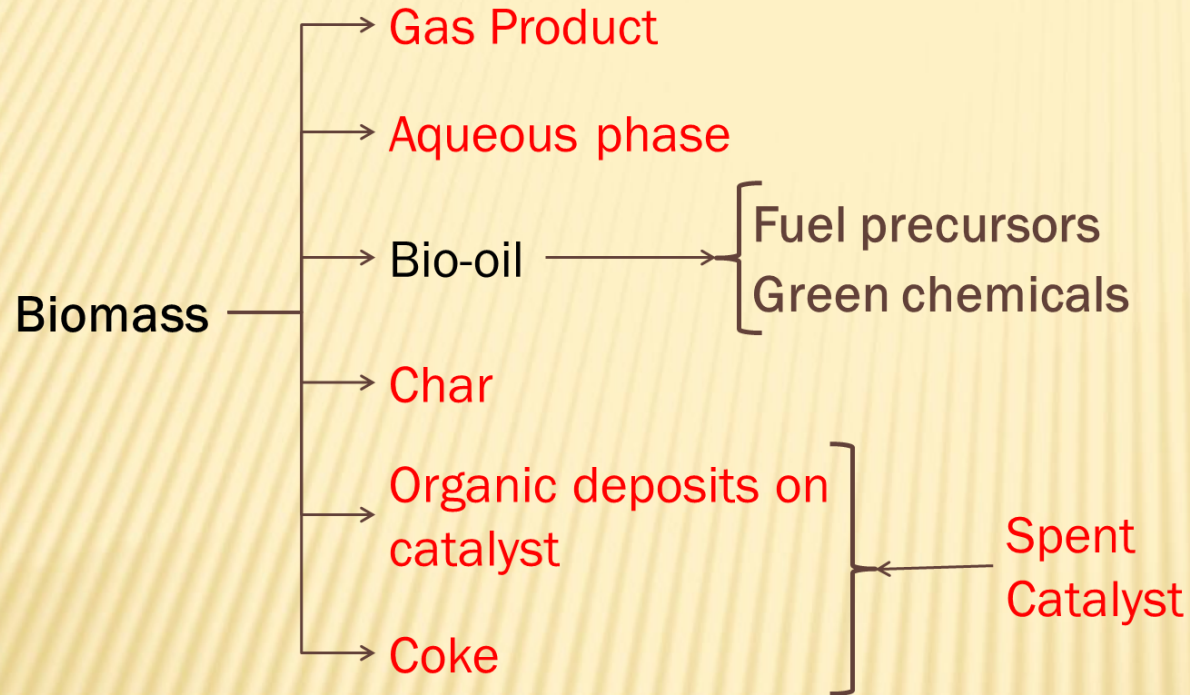
- ✖ Increase C-efficiency
 - + Organics recovery
 - + Organics upgrading
 - + New process chemistry
- ✖ Better catalytic performance
 - + Minimize solid product
 - + Improve physical integrity of catalyst
 - + Improve catalyst stability (decrease deactivation)
- ✖ Environmental and geopolitical drivers
 - + Integrated biorefineries for fuels **and** chemicals
 - + Incentives creation and capture
 - + Development of separation/purification processes
 - + Long-term sustainability



POTENTIAL IMPROVEMENTS

Renewable fuels and green chemicals production

CATALYTIC PYROLYSIS



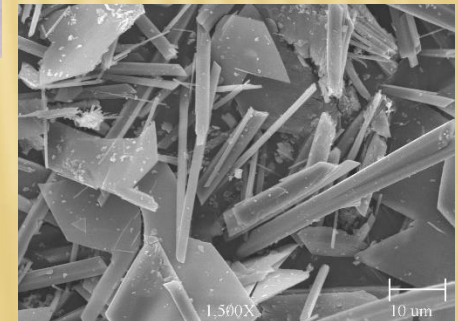
MINERALS

ROLE

- ✗ Increase char formation
- ✗ Promote condensation reactions
- ✗ Deactivate catalyst
- ✗ May affect catalyst integrity
- ✗ Contaminate water
- ✗ Contaminate bio-oil
- ✗ Downstream issues
 - + Deposits / scaling
 - + Corrosion
 - + Plugging

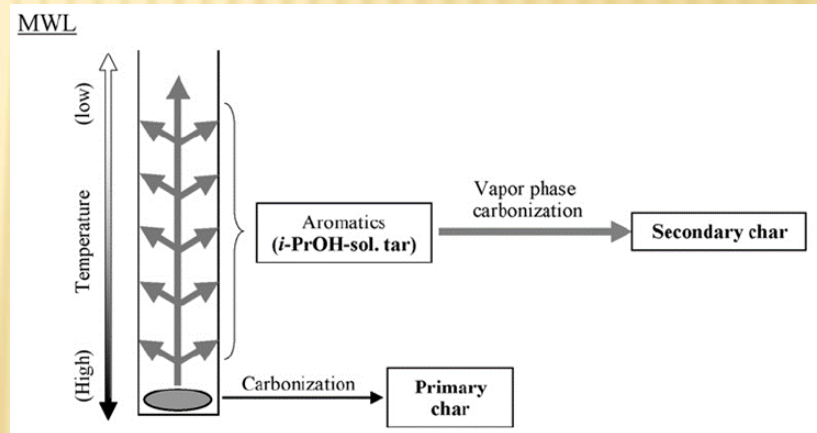
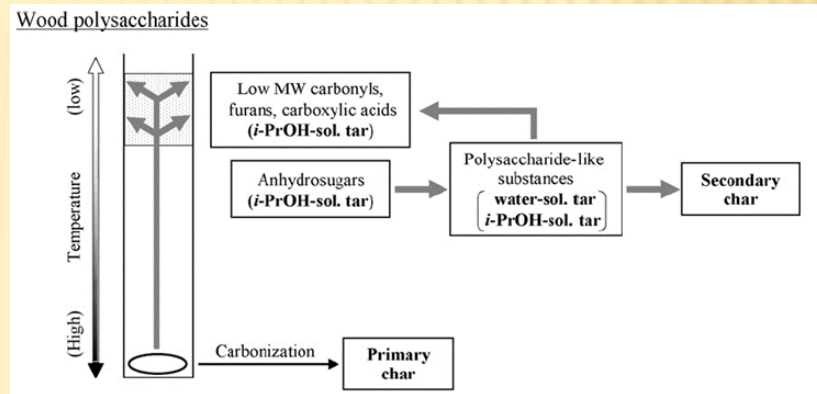
APPROACHES

- ✗ Biomass pretreatment
- ✗ Bio-oil treatment
- ✗ Aqueous phase management
- ✗ Catalyst management



CHAR MAKING: CAN IT BE STOPPED?

- ✗ Minimize H-losses
 - + Minimize dehydroxylation reactions
 - + Improve H-transfer in the gas/vapor phase
 - ✗ H-donors
 - ✗ Direct hydrogenation
 - ✗ Other reactions (e.g. formate addition)
- ✗ Minimize condensation & polymerization reactions
 - + Minerals management
 - + Catalyst functionality
- ✗ Decrease biomass particle size
 - + Pretreatment
 - + Process implications



Sources: T. Hosoya; H. Kawamoto and S. Saka.
Journal of Analytical and Applied Pyrolysis 78
(2007) 328-336; Id. 83 (2008) 71-77

CHANGES IN PROCESS CHEMISTRY: CATALYSTS

- ✖ Increasing throughput: higher activity and broader functionality
- ✖ Reaction selectivity: decrease lights and coke formation, increase DeOx (more decarboxylation and less dehydroxylation).
 - + Lower organic losses into the aqueous phase
 - + Improve HCs miscibility / compatibility
 - + Lower acidity / corrosivity
 - + Facilitate recovery

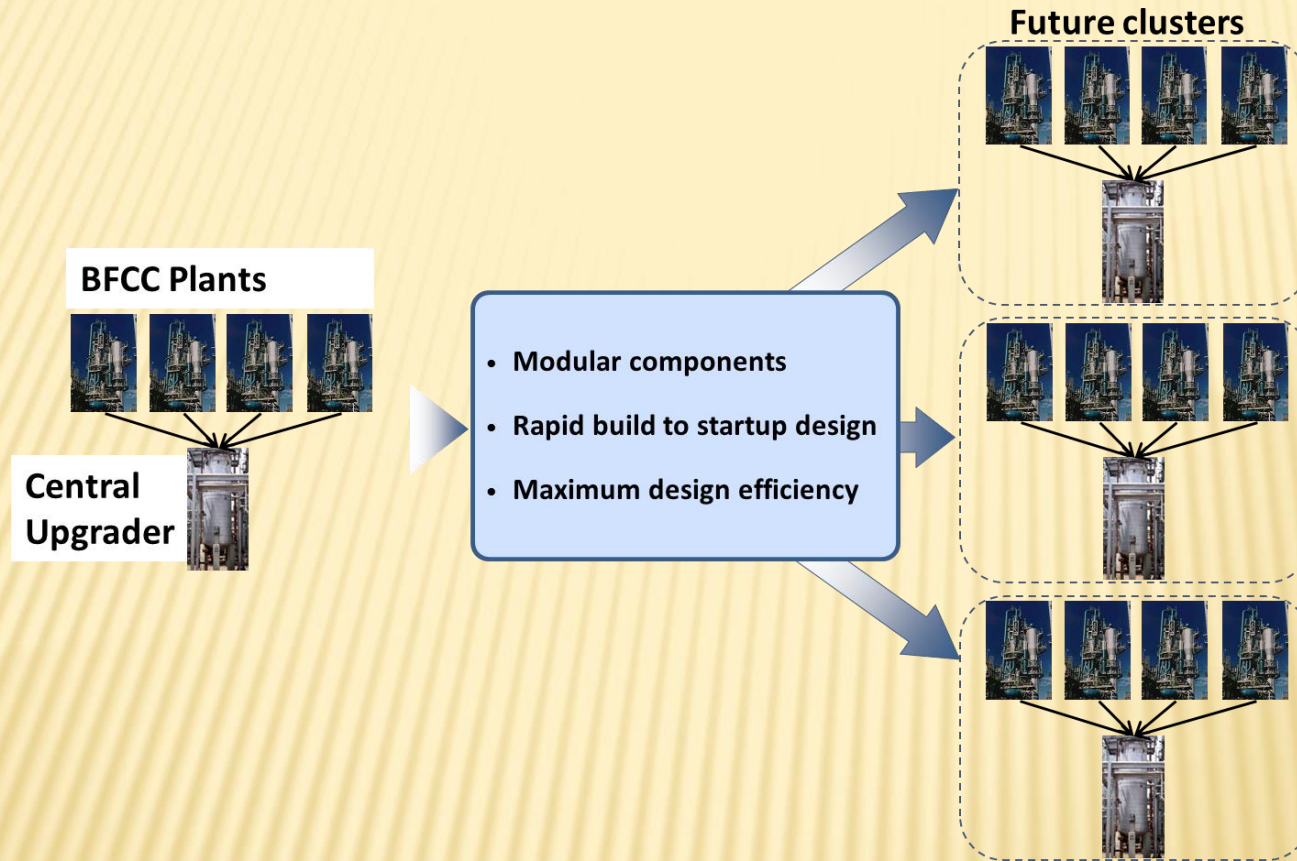


CHEMICALS

- ✖ New processes / routes
 - + Condensation
 - + Heavy acids esterification
 - + Ketonic decarboxylation
- ✖ Product selectivity:
 - + Commercial interest
 - + Functional groups: $-OH$, $-CO$ or $-OMe$
 - + Aromatics & olefins: finished products or building blocks?
- ✖ C-specialties: fibers, nanotubes, adsorbents, soil enhancer?
- ✖ Cost-effective recovery/separation/purification processes

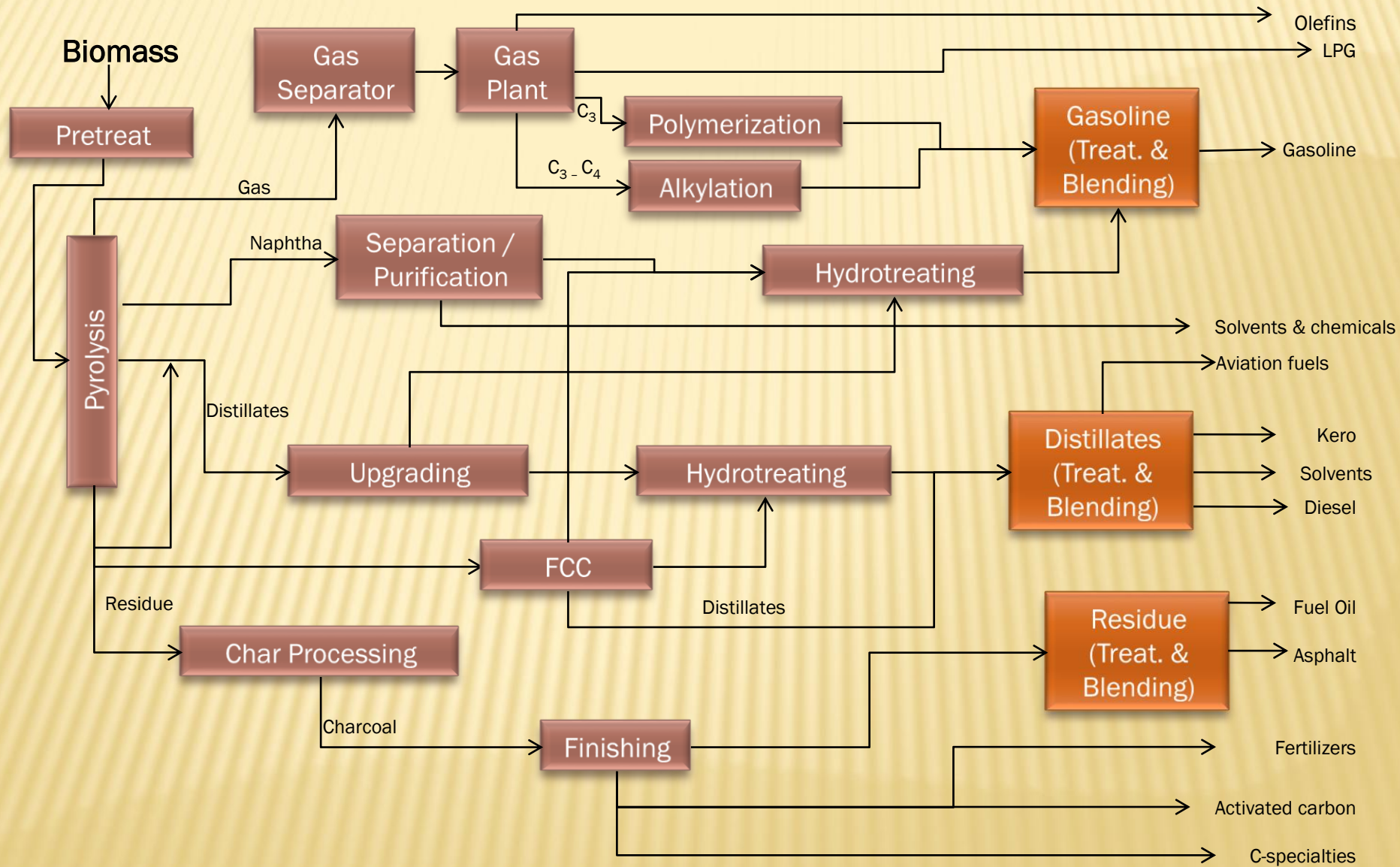


MODULARIZATION STRATEGY



...Repeatable. We plan to employ a modular design for our standard commercial production facilities that can be replicated We believe that this “copy exact” design will help us to reduce our capital costs, implement learned best practices and facilitate rapid deployment of new production facilities...

PYROLYTIC BIOREFINERY



FINAL THOUGHTS

- ✖ Innovations on mature technologies
- ✖ Infancy of emerging technologies: out-of-the-box ideas, even commercial attempts have open the door for innovation on the many problems found.
- ✖ Economic constraints may be addressed by chemical, catalytic and/or process proposals
- ✖ Sustainability may be achieved by intensification and synergetic advantages

....and only sustainable technologies will make history

Thank you!

QUESTIONS?